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(54) **CUPOLA SLAG CEMENT MIXTURE AND METHODS OF MAKING AND USING THE SAME**

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3,230,103 A	1/1966	Minnick
3,565,648 A	2/1971	Mori et al.
4,134,774 A	1/1979	Heese et al.
4,306,912 A	12/1981	Forss
4,369,054 A	1/1983	Shinholster, Jr. et al.
4,377,416 A	3/1983	Maul et al.
4,715,896 A	12/1987	Berry
4,842,649 A	6/1989	Heitzmann et al.
4,964,912 A	10/1990	Okabayashi et al.
4,968,349 A	11/1990	Virtanen
5,073,198 A	12/1991	Kurz

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(60) Provisional application No. 60/183,370, filed on Feb. 18, 2000.

(51) **Int. Cl.**⁷ **B28B 7/10**

(52) **U.S. Cl.** **264/333; 106/714**

(58) **Field of Search** **264/333; 106/714**

(56) **References Cited**

U.S. PATENT DOCUMENTS

1,627,237 A	5/1927	Harding
1,823,928 A	9/1931	Bjorkman
1,831,702 A	11/1931	Cadre
1,916,157 A	6/1933	Chappell
2,248,032 A	7/1941	Dunn et al.
2,248,033 A	7/1941	Wallace et al.
2,446,990 A	8/1948	Schuetz
2,752,261 A	6/1956	Dournaud
2,803,556 A	8/1957	Carlsson et al.
2,947,643 A	8/1960	Kamlet

(List continued on next page.)

FOREIGN PATENT DOCUMENTS

CS	CS 91288	8/1959
DE	19533998	5/1996
DE	19533999	5/1996
RO	115252	12/1999
SU	1250533	8/1986
SU	1413072	7/1988
SU	1416464	8/1988
SU	1744078	6/1992
SU	1759803	9/1992

OTHER PUBLICATIONS

ASTM Designation: C989-99 "Standard Specification for Ground Granulated Blast-Furnace Slag for Use in Concrete and Mortars" (1992).

(List continued on next page.)

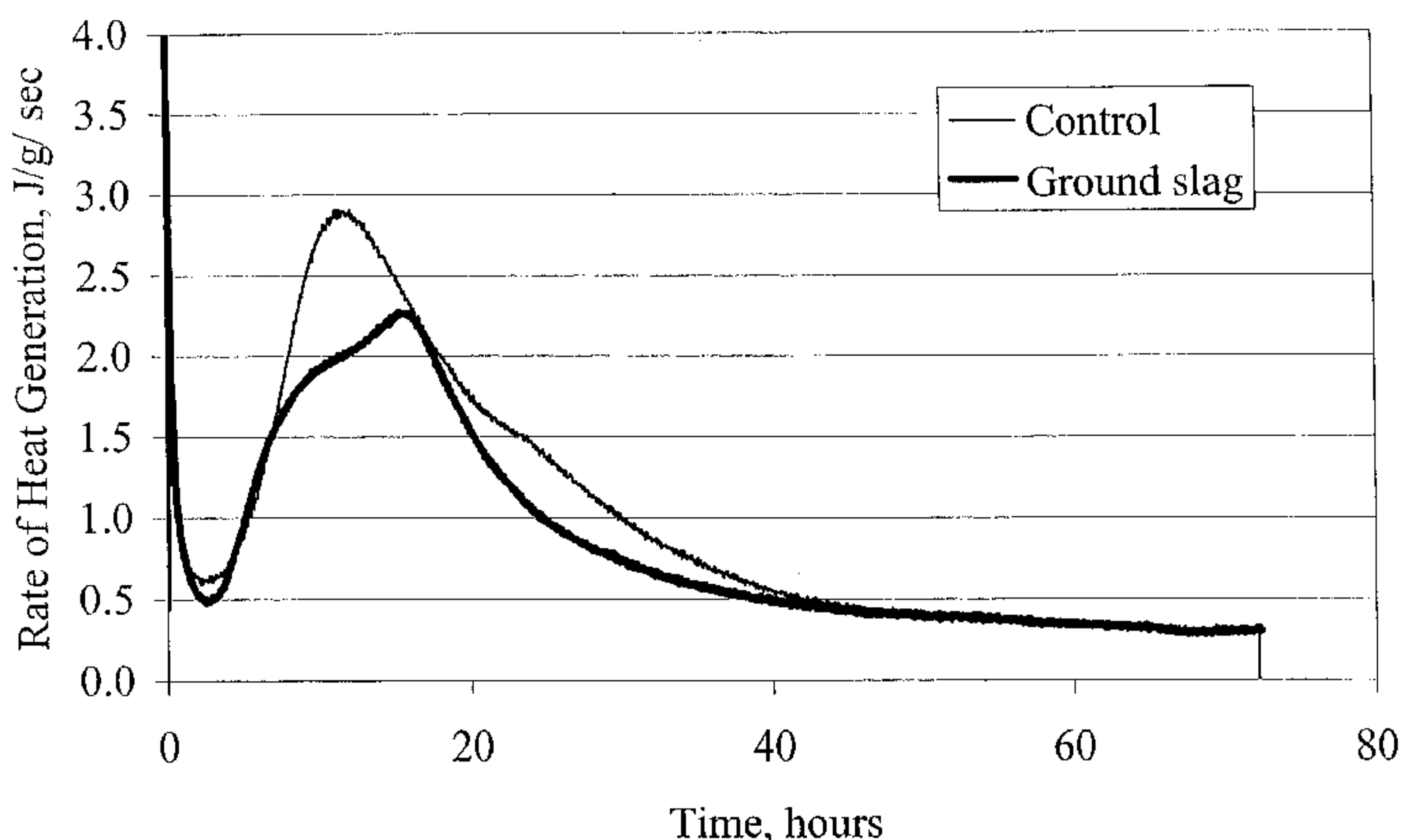
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(57) **ABSTRACT**

A slag cement mixture and process of making the same is disclosed. The slag cement mixture is composed of cupola slag and portland cement. The cupola slag is optionally ground granulated. One embodiment of the process includes rapidly quenching the slag by submersion into water or by spraying water onto it, and grinding the resulting product to achieve a fineness of at least 6,000 cm²/g. The process also includes the addition of 35% ground granulated cupola slag to portland cement to achieve a stronger and harder cement than portland cement alone.

14 Claims, 3 Drawing Sheets



U.S. PATENT DOCUMENTS

5,084,102 A 1/1992 Brouns et al.
5,275,511 A 1/1994 Pelletier et al.
5,311,944 A 5/1994 Cowan et al.
5,346,548 A 9/1994 Mehta
5,374,309 A 12/1994 Piniacki
5,393,342 A 2/1995 Hooykaas
5,395,443 A 3/1995 Hooykaas
5,421,880 A 6/1995 Young
5,473,998 A 12/1995 Allen et al.
5,482,549 A 1/1996 Blaakmeer et al.
5,494,515 A 2/1996 Young
5,553,670 A 9/1996 Cowan
5,556,457 A 9/1996 Terza et al.
5,714,002 A 2/1998 Styron
5,714,003 A 2/1998 Styron
5,766,297 A 6/1998 Piniacki
5,976,243 A 11/1999 Oates et al.
5,997,632 A 12/1999 Styron
6,007,619 A 12/1999 Laas et al.
6,008,275 A 12/1999 Moreau et al.

OTHER PUBLICATIONS

Krivenko et al., "Slag-alkali binders from cupola slag," Building Construction Materials vol. 3-4, pp. 16-17 (1992) Original Russian and English Translation provided.
Krivilev et al., "Use of electric steel-smelting and cupola slag of machine building factories," Tr. Ural. Navchno-Issled. Inst. Chern. Met. vol. 35, pp. 106-108 (1979). Original Russian and English Translation provided.
Sinhamahapatra et al., "Investigation on Granulated Cupola Slag in Cement Making," National Metallurgical Laboratory Technical Journal vol. 8(3), pp. 29-32 (1966).
Lesovik et al., "Slag blocks from foundry wastes," Stroit Mater. Konstr. (1990) 3, p. 15-16.
Fedin et al., "Investigation of Technology of Concrete Containing Cupola Slag and Spend Molding Sand" Stroit. Mater. (1996), (8), 28-39.
Michael Schaaff et al., "Development and testing of an alternative binder system for briquet manufacturing for cupolas," Giesserei (1996), 83 (22), 11-18.

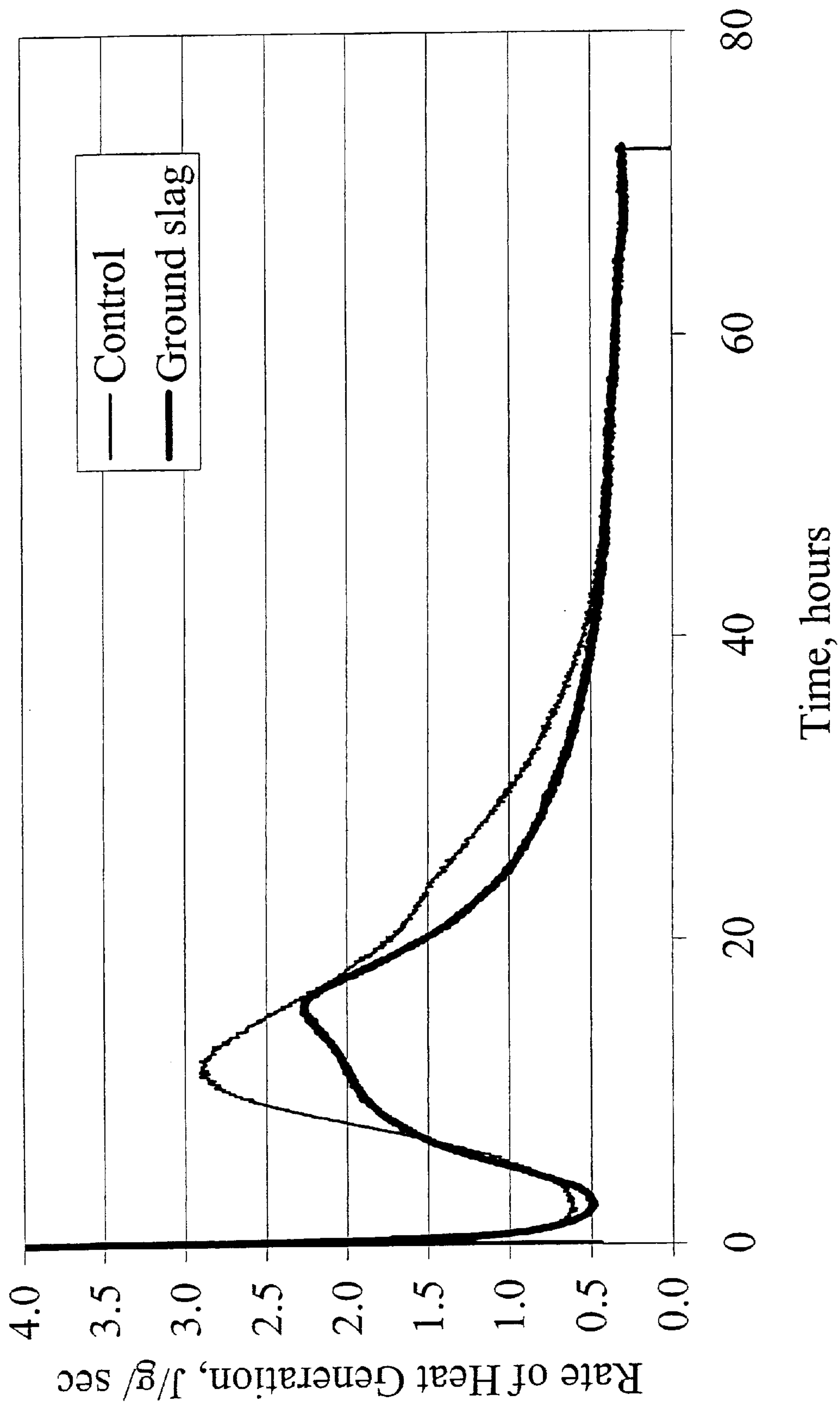


FIG.1

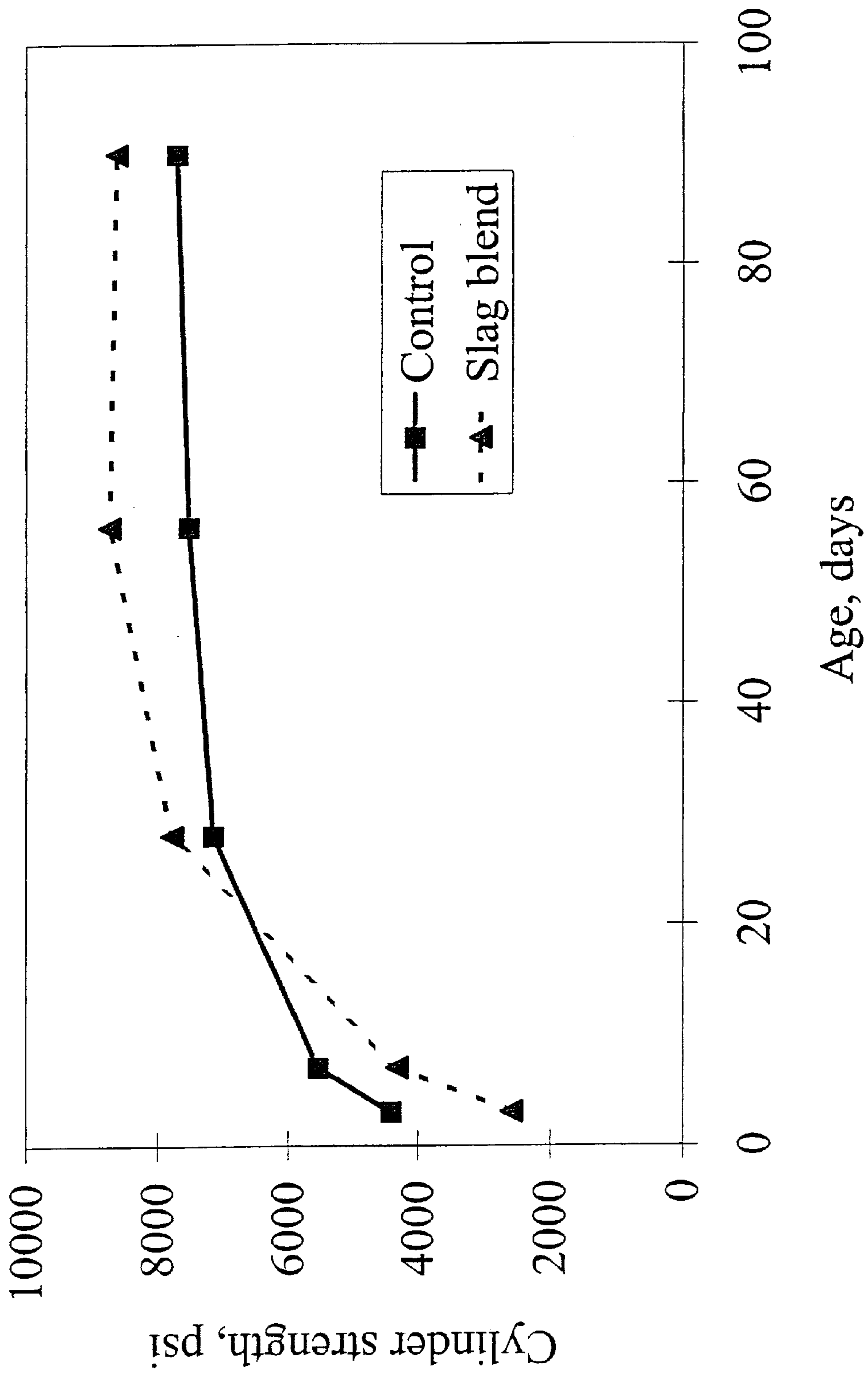


FIG.2

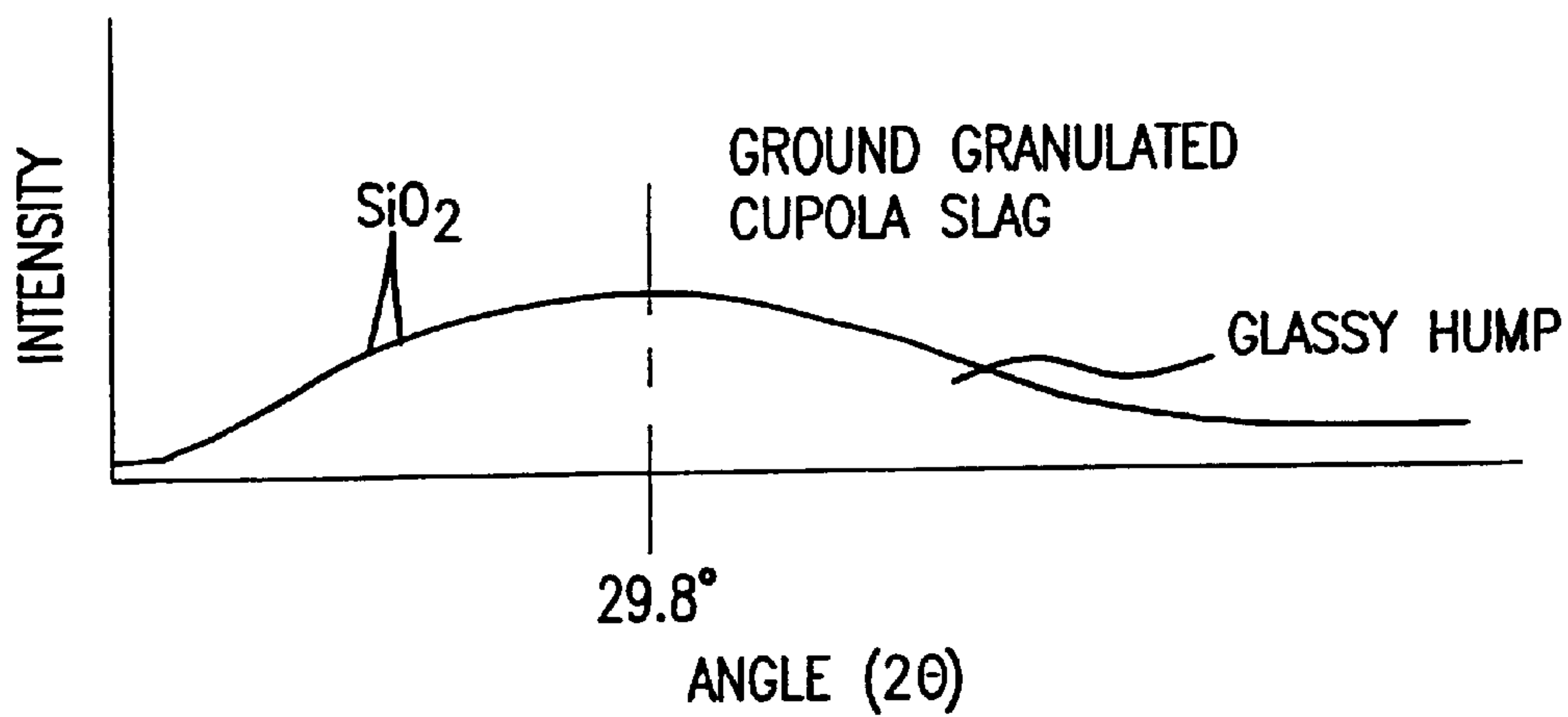


FIG.3A

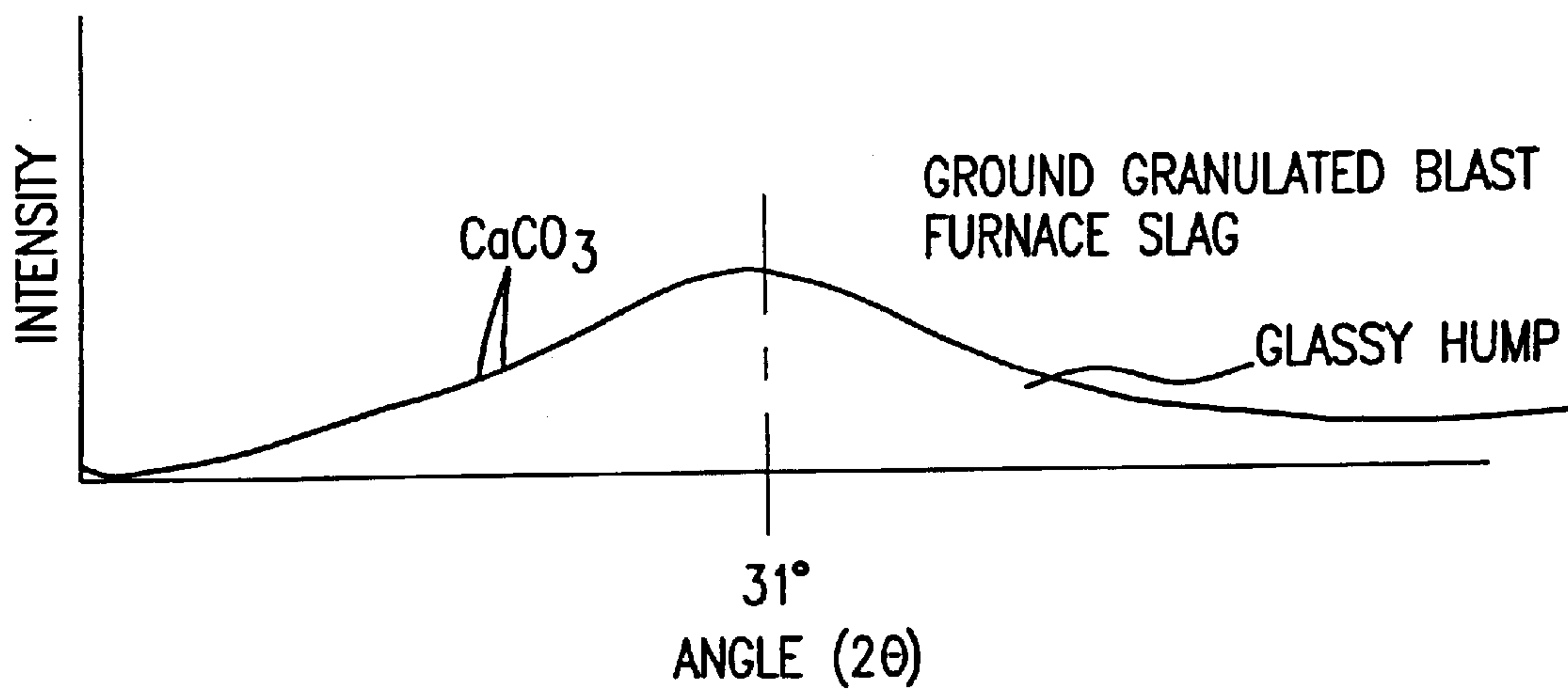


FIG.3B

CUPOLA SLAG CEMENT MIXTURE AND METHODS OF MAKING AND USING THE SAME

RELATION TO PRIOR APPLICATION

This application is a continuation of 09/784,344, filed Feb. 16, 2001, now 6,521,039, which claims priority to U.S. Provisional Patent Application Ser. No. 60/183,370, filed Feb. 18, 2000.

FIELD OF INVENTION

The present invention relates to cement. More particularly, the present invention relates to a slag cement mixture and a process of making the same. While the invention is subject to a wide range of applications, it is especially suited for use in structural concrete and concrete construction.

BACKGROUND

Cement is a widely used building material. A particularly popular variety of cement is portland cement. Portland cement is used in many applications such as mortar, concrete, and cement building materials such as building blocks. Portland cement is produced by pulverizing clinker to a specific surface area of about 3,000 to 5,000 cm²/g or finer. Clinker is created in a cement kiln at elevated temperatures from ingredients such as limestone, shale, sand, clay, and fly ash. The cement kiln dehydrates and calcines the raw materials, and produces a clinker composition comprised of tricalcium silicate (3CaO—SiO₂), dicalcium silicate (2CaO—SiO₂), tricalcium aluminate (3CaO—Al₂O₃), and tetracalcium aluminoferrite (4CaO—Al₂O₃—Fe₂O₃).

Conventional mortar and concrete compositions contain cement, aggregates such as gravel and sand, and water to activate the hydration process. A mortar product is a hardened cement product obtained by mixing cement, a fine aggregate, and water. A concrete product is a hardened cement product obtained by mixing cement, coarse aggregate, water, and often a fine aggregate as well.

The strength properties of concrete and mortar products depend in part on the relative proportions of cement, aggregates, and water. The American Society for Testing and Materials ("ASTM") standard test procedures, such as ASTM C192 and C39 describe the procedures for mixing, casting, curing, and testing portland cement concrete mixtures with 1, 3, 7, 14, and 28 day standards. Greater compressive strength is a desirable feature of cement, and a number of materials have been used to improve the compressive strength of cements.

One way of improving the compressive strength of hardened cement is to blend ground granulated blast furnace slag with cement to give an improved cement composition. Blast furnace slag is a by-product of the production of iron in a blast furnace consisting of silicates and aluminosilicates of calcium. A quick setting cement can be produced by grinding blast furnace slag with gypsum. (See, for example, U.S. Pat. Nos. 1,627,237 and 2,947,643). Blast furnace slag has hydraulic properties very similar to portland cement, and adding blast furnace slag to cement is routine to increase the cement's strength. (See ASTM Specification C989).

Typical North American blast furnace slag composition ranges are 32–40% SiO₂, 7–17% Al₂O₃, 29–42% CaO, 8–19% MgO, 0.7–2.2% SO₃, 0.1–1.5% Fe₂O₃, and 0.2–1.0% MnO. (see The Portland Cement Association

Research and Development Bulletin RD112T). Blast furnaces in the U.S. are operated using a basic slag, typically defined as the slag ratio: (% CaO+% MgO)/(% SiO₂ +% Al₂O₃), where the slag ratio is maintained in excess of 1.0 in order to remove sulfur from the iron produced and to facilitate producing an iron of high carbon content. The chemical composition of blast furnace slag also varies world wide, especially in alumina content. Blast furnace slags have long been recognized as very useful commodities and have been used in a number of applications. In addition to its use as cement additive, blast furnace slag has been used in asphalt, sewage trickle-filter media, roadway fills, and railroad ballast.

Blast furnace slags can be used to prevent excessive expansion of concrete mixtures that have a high-alkali content and aggregates that are alkali-reactive. Use of blast furnace slag as 40% or more of such a cement mixture can prevent excessive expansion. Blast furnace slag is characterized by its short setting time, which is the time between the addition of mixing water to a cementitious mixture and when the mixture reaches a specified degree of rigidity as measured by a specified procedure.

Steel slag is also used as a cement additive. Steel slag is formed in the process of making steel in a blast furnace, and often has a high concentration of ferrites. Because of its high ferrite composition, steel slag is generally used as a filler in cement road building material or as a feedstock raw material in cement kilns. It is possible to produce a hydraulic cement base from steel slag by adding further minerals to the slag portion, thereby reducing the ferrite composition of the slag. This additional step, while rendering a usable product, is costly and time consuming.

Mixtures of blast furnace slag and steel slag have resulted in stronger cement products, but cupola furnace slag, a by-product of cast iron production, is only rarely used in cement except as a processing addition. (See ASTM C465 and Cupola Handbook, published by the American Foundrymen's Society). Blast furnaces and cupola furnaces are operated differently and are used to make different iron products, consequently, the slag products of these furnaces are also different, both in chemical composition and in material properties. Cupola slag has different hydraulic properties than blast furnace slag. For example, cupola slag blended cement sets more slowly and at 7 days lacks the strength of blast furnace slag blended cements. Also, cupola slag is not a common concrete additive due to environmental concerns such as the possibility of rain water leaching out some of its components. Indeed, cupola slag often presents a disposal problem, which creates an additional expense, ultimately increasing the cost of the iron produced.

There is an ever present need in the cement art for harder, stronger cement products with longer setting times. There is also a need in the cast-iron production art for a disposal method for cupola slag that is environmentally safe and economically practical.

SUMMARY OF THE INVENTION

Accordingly, the present invention is directed to a cupola slag blended cement with an increased compressive strength. The principal advantage of the present invention is a cement mixture that results in a concrete which is both harder and stronger while providing a means of recycling cupola slag that is both environmentally sound and economically practical. The cement compositions of the present invention have a resistance to expansion due to sulfate attack and alkali silica reaction, and can be formulated to have a wide range of curing times.

To achieve these and other advantages and in accordance with the purpose of the invention, as embodied and broadly described, the invention is a hydraulic cement containing cupola slag ground to a fineness of greater than 4,000 cm²/g blended with portland cement. A preferred embodiment of the invention is a hydraulic cement containing cupola slag ground to a fineness of greater than 5,000 cm²/g blended with portland cement. In the most preferred embodiment, the invention is a hydraulic cement containing cupola slag ground to a fineness of between 6,000 cm²/g and 7,000 cm²/g.

In one embodiment, the invention is a hydraulic cement containing from about 20 to 50% of a ground granulated cupola furnace slag blended with portland cement. In a preferred embodiment, the invention is a hydraulic cement containing from about 30% to 40% cupola slag blended with portland cement. In another preferred embodiment, the invention is a hydraulic cement containing about 35% cupola slag blended with portland cement.

The invention includes ground granulated cupola furnace slag with a fineness of about 5,000 to about 7,000 cm²/g and meeting the fineness requirement of the ASTM C989 Grade 100 specification for blast furnace slag.

The invention includes ground granulated cupola furnace slag with a fineness of about 6,000 to about 6,750 cm²/g. The invention also includes ground granulated cupola furnace slag with a fineness of about 6,500 cm²/g.

In one embodiment of the invention, a blended cement mixture of about 35% cupola furnace slag displays a 28 day compressive strength of more than 7,000 psi and a flexural strength of more than 700 psi.

In another embodiment of the invention, the total heat of hydration of the blended cement mixture of about 35% cupola furnace slag does not exceed 250 J/g when measured for 72 hours, and the expansion of mortar bars does not exceed 0.20% at when measured at 14 days.

In one embodiment, the invention includes a process of using cupola slag as a raw cement kiln feedstock.

BRIEF DESCRIPTIONS OF THE DRAWINGS

FIG. 1 shows the results of conduction calorimetry tests performed on two neat cement pastes: standard portland cement (darker line), and a portland cement/cupola slag blend (lighter line).

FIG. 2 shows the results of compressive strength tests performed on concrete objects made with the same aggregates, but using either standard portland cement (solid line), or a 65/35% blend of portland cement and cupola slag (dashed line).

FIGS. 3a and 3b show the results of X-ray powder diffraction tests performed on cupola furnace slag (upper diffractogram) and on blast furnace slag (lower diffractogram).

DETAILED DESCRIPTION OF THE INVENTION

The present invention encompasses blends of cupola slag and cement with an increased hardness and strength than the cement alone.

The hydraulic cement compositions of the present invention provide a solution to the current needs of the art by converting cupola furnace slag into a useful product. The cement compositions of the invention can be formulated to have a wide range of resistance to sulfate attack as well as wide range of curing times so that they can be used for a

variety of purposes such as making concrete objects. In particular, a hydraulic cement containing 35% of a ground granulated cupola furnace slag, with a fineness of at least 6,000 cm²/g and meeting the fineness requirement of the ASTM C989 Grade 100 specification for blast furnace slag blended with portland cement creates a composition whose superior compressive strength develops slower than the concretes currently in use thus providing a more durable concrete product. Additionally, the sulfate attack resistance of the present invention increases the useful life of any products made from cupola furnace slag blended cements thereby increasing the length of time between replacing such products and reducing the overall cost of any such project.

The chemical composition of portland cement plays an important role in the way that slag blended cements cure, age and resist chemical attack. The processing of portland cement is well known in the art, as are the various methods to alter the chemical composition during the manufacturing process. The invention is not, however, limited to portland cement. It is believed that cupola slag mixed with other cements will improve the strength of the cement/cupola slag mixture.

A cupola furnace is a vertical shaft furnace used to produce cast iron by high temperature melting of metallic and mineral charge materials. A cupola furnace contains a continuous melting shaft which can accept a wide range of raw materials including oily, wet and contaminated scrap. Compared to batch-type furnaces, the energy requirements of a cupola furnace are low. Molten iron is tapped from the bottom of the furnace. Slag is removed in a molten state via a slag hole. Cupola furnace slag is preferably rapidly quenched by submersion into water to yield a fine, granulated product, thus reducing the amount of grinding required to make the slag useful in cement. Alternatively, water may be sprayed upon the slag to quench it, or the slag may be allowed to air-cool for a time, resulting in a coarser, non-granulated product.

Cupola furnace slag differs from blast furnace slag in chemical composition; for example, cupola slag has a higher silica content and a lower calcium oxide content than blast furnace slag. While blast furnaces operate using a basic slag, cupola furnaces generally operate using an acid slag for the production of gray cast iron. (Basic slags are sometimes used in cupola furnaces for the production of ductile iron because the basic slag removes sulfur in the cupola during melting). Blast furnace operations produce about 30 percent slag per ton of molten iron, while cupola furnace operations produce 5 to 6 percent slag per ton of iron ore that is melted.

Cement users are particularly interested in setting and strength development characteristics. The maximum and minimum setting times and minimum strengths of reference cement are specified in the ASTM C150 standard specification for portland cements. A number of minor components which form in the clinker from impurities present in the raw materials or fuel can influence both the clinker formation process and the hydraulic reactivity and cementitious properties of the resulting cementitious material. In particular, the level of alkalis, such as K₂O and Na₂O present in cement, especially portland cement, may be of concern. For example, if the cementitious materials are combined with aggregates containing SiO₂, the alkalis present in the cementitious materials may react with the SiO₂ to form an expansive alkali silica gel, which can lead to cracking and break up of the concrete structure. Because the detection of reactive SiO₂ in aggregates is difficult, cementitious materials with low alkali content are generally used. Blast furnace slags are generally very basic in nature. Thus, a

maximum equivalent Na_2O of about 0.6 percent is included as an optional limit in the ASTM C150 specification.

It is possible to use cement containing more than 0.60 percent equivalent Na_2O with SiO_2 reactive aggregates while avoiding excessive expansion and reducing the total energy used to manufacture the cement. One example is to mix cement, preferably portland cement, with latently hydraulic materials such as ground granulated blast furnace slag. However, the latently hydraulic materials do not react as quickly as portland cement, and as a result they contribute to the later developed cement strength rather than the earlier. The decreased early activity results in lower heats of hydration, which leads to thermal crack formation. However, the addition of blast furnace slag does not eliminate thermal crack formation.

ASTM C125-99a "Standard Terminology Relating to Concrete and Concrete Aggregates" defines a number of terms that apply to hydraulic cement. It is well known in the prior art, that the hydraulic properties of blast furnace slag vary greatly upon the chemical nature of the blast furnace slag and the way that molten slag is cooled.

Blast furnace slag is classified by performance in the blast furnace slag activity test in three grades, Grade 80, Grade 100, and Grade 120. ASTM specification C989 outlines the strength development of portland cement mixed with the three strength grades of finely ground, granulated blast furnace slag as measured at seven days and twenty-eight days and expresses this as blast furnace slag activity index (SAI). When blast furnace slag is used in concrete with portland cement, the levels and rate of strength development depend on the properties of the blast furnace slag, the portland cement, the relative and total amounts of the blast furnace slag and the cement as well as the cement curing temperatures. Unless the slag is derived from a blast furnace it cannot be marketed as blast furnace slag under the ASTM C989 standards.

ASTM C989 specifies that the reference cement used to test blast furnace slag activity have a minimum 28-day strength of 35 MPa (5,000 psi) and an alkali content between 0.6 and 0.9%. To properly classify a blast furnace slag, the reference portland cement must conform to the limits on strength and alkali content under ASTM specification C989. Test data indicate that concrete compressive strengths at 1, 3 and even 7 days tend to be lower using blast furnace slag cement combinations. Generally a higher numerical grade of blast furnace slag can be used in larger amounts and will provide improved early strength performance, but tests must be made using job materials under job conditions to properly access the performance of a blast furnace slag cement.

Blast furnace slag has latent hydraulic properties that require an activator to realize these hydraulic properties. One way for slag to acquire hydraulic properties is to rapidly quench the slag to preserve the molten slag in a vitreous state. Two processes that are commonly used to activate the slag's hydraulic properties are granulation and pelletization. In the granulation process, slag is quenched by the injection of a large quantity of water under pressure into the slag. If the temperature of the slag is above its melting point prior to quenching, then quenching produces a wet sand-like material with a high degree of vitrification. But if the slag is permitted to cool slowly, it crystallizes and exhibits reduced hydraulic properties. To achieve the desired fineness, the granulated slag is dried and ground. Blast furnace slags are typically ground to a specific surface area of 5,000 to 6,500 cm^2/g . A fineness of greater than 6,500 cm^2/g requires additional steps and is more difficult to achieve on a large

industrial scale under dry conditions. Another measure of specific surface area is the Blaine air permeability method. The Blaine Fineness test is described in ASTM C204 "Standard Test Method of Hydraulic Cement by Air Permeability Apparatus." There, blast furnace slags are described as having a specific surface area of 5,000 to 6,500 cm^2/g . The early development of high strength is a characteristic of cements comprising blast furnace slag ground to a fineness of 7,500 cm^2/g . As the fineness increases so does the rate of the hardening reaction. As ground granulated blast furnace slag typically has a fineness of about 5,000–6,500 cm^2/g , an extra grinding step is required to achieve a fineness of 7,500 cm^2/g . There is an energy cost for the extra grinding step, but it substantially improves the mechanical strength of the resulting cement. Greater specific surface areas generally result in greater initial strengths.

Cupola furnace slag can be granulated by the process of slag quenching. Molten cupola furnace slag is granulated by the injection into the slag of a large quantity of water under pressure, producing a wet sand like material with a high degree of vitrification. The degree of vitrification depends on the slag temperature prior to injection and the temperature of the water under pressure. Because cupola slag has a lower sulfate and magnesium content and a higher silica and iron oxide content there is a decrease in the heat generated, which is advantageous for increasing setting time and slowing the initial strength gain of the concrete. The lower sulfate and magnesia content coupled with a higher silica and iron oxide content also leads to a reduction in the expansions due to heat of hydration and alkali silica reaction.

For the purpose of illustrating the advantages obtained by the practice of the present invention, plain concrete mixes were prepared and compared to similar mixes containing cupola slag. The following example is illustrative and is not intended to be limiting. The methods and details were in accordance with current applicable ASTM standards.

EXAMPLE 1

Cupola furnace slag useful in cement compositions of the present invention desirably shows the following components upon analysis:

TABLE 1

Composition of Cupola Slag	
Component	Proportion (wt. %)
SiO_2	43.87
Al_2O_3	8.5
Fe_2O_3	1.93
CaO	33.3
MgO	3.38
SO_3	0.30
Na_2O	0.10
K_2O	0.30
TiO_2	0.34
P_2O_5	<0.01
Mn_2O_3	1.18
SrO	0.08
L.O.I. (950° C.)	4.34
Total	97.84
Alkalies as Na_2O	0.30

Although only applicable to blast furnace slag, the Slag Activity Index test as described in ASTM C989 "Standard Specification for Ground Granulated Blast Furnace Slag for Use in Concrete" was performed on the cupola furnace slag as well as a Blaine Fineness test as described in ASTM C204 "Standard Test Method of Hydraulic Cement by Air Perme-

ability Apparatus." Table 2 shows the results of these two tests for two different cupola slag samples ground using a 40-lb mill to two different fineness values similar to those of commercially available blast furnace slags.

TABLE 2

Fineness and Slag Activity Index data				
	Ground Cupola Slag Sample		ASTM C989 Requirement for:	
	No. 1	No. 2	Grade 80 min	Grade 100 min
Fineness, cm ² /g	4240	6530	—	—
Slag Activity At 7 days	61	73	—	70
Index, % of At 28 days control	98	124	70	90

As evident from Table 2, both samples exceeded the ASTM C989 SAI requirements for Grade 80 and Grade 100 blast furnace slag at 28 days. Sample 2 met the SAI 7 day requirements for Grade 100 as well. Based on this test, all additional tests were preformed on Sample 2

Conduction calorimetry tests were conducted on neat cement pastes made with the control cement and with cupola furnace slag blend by injection-mixing of 2 grams of cement with water inside a calorimeter cell. The slag used in this test was Sample 2 as it met the ASTM C989 Blast Furnace Slag Activity Index requirement for 7-day and 28-day of commercially available blast furnace slag Grade 100. The heat of hydration was recorded over a 72 hour period. The first peak represents the heat reaction as the cement comes into contact with the mix water. After the initial peak there is a period of relative inactivity during which the paste remains plastic. The second peak indicates an accelerated reaction during which the alite in the cement hydrates rapidly and heat is generated. The initial setting of the paste occurs soon after the beginning of the acceleration period and the final setting occurs towards the end of the acceleration period. A maximum in heat evolution is reached soon after the final set, after which the heat evolution declines to a steady state. The heat of hydration is a function of both the chemical and the physical properties of the cement. Table 3 shows the results of the calorimetry tests.

TABLE 3

Heat Generation Data for Portland Cement and Cupola Furnace Slag Blended Cement						
Description	Control			Cupola Slag Blend		
	Time	Rate of heat generation J/Kg/sec	Total Heat J/g	Time	Rate of heat generation J/Kg/sec	Total Heat J/g
Initial Hydration Peak	2.28 min	48.74	3.35	3.48	23.55	2.51
Total Heat at:	0.5 hr		15.43	0.5 hr		11.07
Onset of Alite Hydration Peak	2.15 hr	0.59	20.15	3.09 hr	0.51	17.26
Alite Hydration Peak	11.20 hr	2.91	71.17	15.30 hr	2.70	89.28
Total Heat at:	24 hr		169.61	24 hr		140.91

TABLE 3-continued

Heat Generation Data for Portland Cement and Cupola Furnace Slag Blended Cement						
Description	Control			Cupola Slag Blend		
	Time	Rate of heat generation J/Kg/sec	Total Heat J/g	Time	Rate of heat generation J/Kg/sec	Total Heat J/g
Total Heat at:	48 hr		235.70	48 hr		193.40
Total Heat at:	72 hr		264.33	72 hr		223.19

Table 3 indicates that the initial hydration peak for cupola slag cement occurs later in time than that of the control cement and generates heat at a much slower rate and generates a lot less heat. Total heat one half hour after hydration is considerably lower for cupola furnace slag as well. Another major difference between the control cement and the cupola furnace slag cement is that the onset of alite hydration and the peak of hydration are both much later in the cupola slag cement than in the control. Initially the total heat released for alite hydration is lower for the cupola slag cement but by the time the peak of alite hydration occurs, the total heat generated is higher for the cupola slag cement than the control cement. Total heat released overall remains lower for the cupola slag cement at each of the time periods measured. It is anticipated that the surprising low-heat properties of the cupola slag cement will make it particularly useful in making concrete that is adapted for mass concrete pours such as raft foundations, bridge decks, piers, and dams.

Resistance to sulfate attack on Sample 2 was tested in accordance with ASTM C1012 "Standard Test Method for Length Change of Hydraulic-Cement Mortars Exposed to a Sulfate Solution". The expansion of the control and the blended cupola furnace slag cement at 15 weeks was 0.026 and 0.015% respectively.

The potential for the cupola slag to modify alkali reactivity was determined using ASTM C1260 "Standard Test Method for Potential Alkali Reactivity of Aggregates (Mortar Bar Method)". The cement used in this test was the cupola furnace slag bend of sample 2, and the aggregate was a highly reactive graded Albuquerque sand. Table 4 shows the results.

TABLE 4

Expansion of Bars Due to Alkali Silica Reaction			
Age, Days	Expansion, %		
	Control	Cupola Slag Blend	
0	0.000	0.000	
5	0.009	0.013	
11	0.349	0.77	
14	0.580	0.195	

Table 4 indicates that the potential of cupola slag to modify alkali reactivity is considerably lower for cupola slag at days 11 and 14 than the control.

Compression and flexural strengths of a blended cement containing 35% cupola furnace slag (Sample 2) was measured at day 3, day 7, day 28, day 56 and day 90 and compared to a control cement measured with the same age

in days. No chemical additives were added to either and the mixes were made with the same cementitious content as well as the same water to cementitious ratio. The mix portions of the two cements are shown in Table 5 while the results of the compression and flexural tests are shown in Table 6.

TABLE 5

Material	Concrete Mix Proportions	
	Mix Proportions	
	Control	Cupola Slag Blend
Portland Cement, pcy*	654	426
Slag, pcy	0	229
Eau Claire sand, pcy	1,342	1,336
Eau Claire ¾" stone, pcy	1,847	1,849
Water, pcy	266	267
Slump, inches	5	7

(*pounds per cubic yard)

TABLE 6

Age, Days	Compressive and Flexural Strength Results			
	Compressive Strength (ASTM C39), psi		Flexural Strength (ASTM C78), psi	
	Control	Cupola Slag Blend	Control	Cupola Slag Blend
3	4,410	2,570	—	—
7	5,530	4,320	785	490
28	7,150	7,780	750	755
56	7,530	8,740	770	750
90	7,710	8,630	—	—

Table 6 demonstrates that the cupola slag blended cement at days 3 and 7 displays a lower compressive strength when measured using the ASTM C29 method. By day 28, however, the compressive strength of the cupola slag has surpassed that of the control cement, a totally unexpected result. Additionally, the compressive strength of the cupola slag blended cement unexpectedly continued to increase until after day 56 where it begins to level off. At day 56 the compressive strength of the cupola slag blended cement is more than 1,200 psi greater than the control cement. These tests indicate the surprising result that the cupola slag blended cement makes superior concrete over that made with conventional cements. Table 6 demonstrates that the flexural strength of the cupola slag blended cement as measured by the ASTM C78 method develops at a slower rate than that of the control but after 28 days is approximately equal to that of the control cement.

X-RAY DIFFRACTION ANALYSIS

X-ray diffraction may be used to identify and quantify crystalline materials. Crystalline materials consist of ordered arrangements of atoms in three-dimensional arrays. Such arrays have characteristic spacings between the layers of closely packed atoms. The length of the spacings vary by atom size and the three dimensional arrays.

When a powdered sample is subjected to a beam of radiation from an X-ray source a diffraction pattern is created. The X-ray beam penetrates the powder a short distance and diffracts from the most densely packed layers of the atoms within the powdered sample. The X-ray beam is rotated through a series of angles relative to the surface of the powdered sample. When the signal from the diffracted

beam is particularly strong, the distances between layers of atoms (the d-spacings) can be calculated as multiples of the wavelengths of the incident radiation and the incident angle.

A crystalline material has a characteristic pattern of relative peak heights at given angles. Mixtures of crystalline materials display combinations of these patterns and the relative peak heights from various materials can be used to quantify the relative concentration of each crystalline material. X-ray diffraction may also be used to identify cracks in concrete. The detection limit for X-ray will depend on the type of material analyzed and it can be as high as 5 to 10%.

A ground granulated cupola furnace slag sample was finely powdered and subjected to XRD analysis on a Philips PW 1720 X-ray diffractometer (CuK θ) equipped with a θ -compensating slit, graphite monochromator, gas proportional counter detector, pulse height selector and a strip chart recorder. A commercial granulated blast furnace slag sample was also finely powdered and analyzed as a control. Each sample was scanned from 65°2 θ to 6°2 θ at a rate of 1°2 θ per minute. Table 7 is a summary of the phases detected by XRD.

TABLE 7

Sample	X-ray Diffraction Analysis	
	Largest Phase Detected	Crystalline material
Cupola Furnace Slag	Amorphous material with a peak at 29.8° 2 θ	SiO ₂ (α -quartz)
Blast Furnace Slag	Amorphous material with a peak at 31° 2 θ	CaCO ₃ (calcite)

As can be seen from Table 7, the two slag samples vary in their crystalline composition as well as their non-crystalline or glassy composition. The cupola slag sample has an amorphous phase peak at 29.8°2 θ (lower angle) indicating a larger d-spacing than that of the blast furnace slag. The XRD analysis also shows that crystalline SiO₂ is present in the cupola slag which suggests a more acidic form of the amorphous phase. The amorphous phase of the cupola slag probably contains of higher amounts of not only SiO₂ but also Al₂O₃ and Fe₃O₃ than the blast furnace slag.

All references and standards cited herein are incorporated in their entireties.

What is claimed is:

1. A method for making a hardened cement product with improved strength comprising the steps of:

blending cupola slag with a hydraulic cement, wherein the cupola slag is ground to a fineness greater than 4,240 cm²/g,

adding water, and curing.

2. The method of claim 1, wherein the cupola slag is ground to a fineness greater than 5,000 cm²/g.

3. The method of claim 2, wherein the cupola slag is ground to a fineness greater than 6,000 cm²/g.

4. The method of claim 2, wherein the cupola slag is ground to a fineness of between 6,000 cm²/g and 7,000 cm²/g.

5. The method of claim 4, wherein the cupola slag is ground granulated.

6. The method of claim 3, wherein the cupola slag comprises between 32% and 45% SiO₂, between 7% and 17% Al₂O₃, between 29% and 42% CaO, and between 2% and 19% MgO.

7. The method of claim 3, wherein the hydraulic cement is portland cement.

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8. A method for making a hardened cement product with improved strength comprising the steps of:

blending between 5% and 50% by volume of cupola slag with a hydraulic cement, wherein the cupola slag is ground to a fineness greater than 4,240 cm²/g, adding water, and curing.

9. The method of claim **8**, comprising between 20% and 40% by volume of cupola slag.

10. The method of claim **9**, comprising about 35% by volume of cupola slag.

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11. The method of claim **8**, wherein the cupola slag is ground to a fineness of greater than 5,000 cm²/g.

12. The method of claim **11**, wherein the cupola slag is ground to a fineness of between 6,000 cm²/g and 7,000 cm²/g.

13. The method of claim **12**, wherein the cupola slag is ground granulated.

14. The method of claim **13**, wherein the hydraulic cement is portland cement.

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